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DIFFUSION AND SUPERSATURATION IN GELATINE.

By Harry W. Morse and George W. Pierce.

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I. Introduction.

The German photographer, R. Ed. Liesegang, in the course of a research on chemical reactions in gelatine,* discovered a phenomenon which Ostwald cites as evidence that there exists a definite limit beyond which, at a given temperature and pressure, the supersaturation of a solution cannot be carried. We have undertaken an experimental study of this subject by a method based on Liesegang's discovery.

Liesegang's experiment was as follows: A glass plate was covered with gelatine impregnated with potassium chromate. The plate was laid horizontal, and upon it a drop of silver nitrate was placed. The silver nitrate diffused slowly out into the gelatine, reacted with the potassium chromate, and formed a precipitate of silver chromate. The silver chromate, instead of growing continuously in the gelatine, as diffusion of the reacting substances went on, formed in distinct *rings* about the drop, as shown in Figure 1. The formation of the precipitate in distinct rings is clearly a phenomenon of supersaturation. We have undertaken certain measurements of these rings in the hope of being able to obtain from them some understanding of the conditions that exist in supersaturated solu-

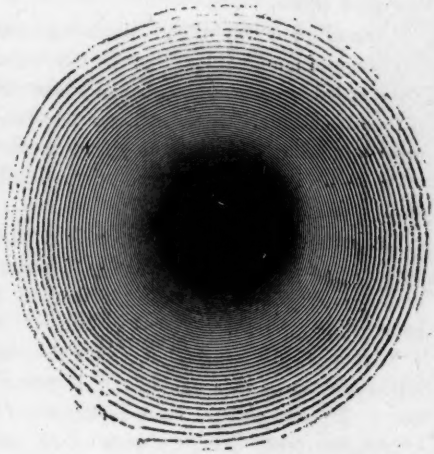

Figure 1.

* Chemische Reactionen in Gallerten. Düsseldorf, 1898.

tions. In particular we have set for ourselves the problem to calculate from these rings the rate of diffusion of the reacting substances, and to estimate the limit of supersaturation attained when the solid phase is not present, — the so-called "Metastable Limit" of Ostwald.

Before proceeding to the experiments we shall give certain definitions and explanatory paragraphs from Ostwald's Lehrbuch.*

"Between a solid substance and its supersaturated solution an equilibrium is formed, which depends on the nature of the substances, the temperature, and the pressure. If we leave out of account the influence of the pressure, for every temperature there is a definite equilibrium. This is evidenced by a definite concentration up to which the solid substance dissolves. . . .

"When the solid phase is not present, the concentration of the dissolved substance is arbitrary. The limit of concentration on one side is zero; on the other side the limit is a concentration difficult to determine, which, however, is greater than that of the equilibrium with the solid phase.

"Solutions whose concentrations exceed the concentration of saturation with a possible solid phase are called supersaturated with reference to this solid phase. . . .

"The simplest way of obtaining a supersaturated solution is to produce by change of temperature from the solid substance and the solvent a solution that is more concentrated than a saturated solution at the temperature of the experiment. In most cases the temperature required to produce supersaturation is higher than the temperature of the experiment, but it can also be lower in cases where the solubility decreases with increase of temperature.

"A better way to obtain supersaturated solutions, since it is thereby easier to exclude germs of the solid phase, is to employ reactions that produce in the solvent concentrations of the substance in question in appropriate amount.

"Among supersaturated solutions there are some which under definite conditions can be kept indefinitely, if germs are excluded, without formation of the solid phase. Such solutions are called Metastable.

"On the other hand, there are some solutions in which, even when germs are excluded, the solid phase appears after a short time. Solutions of this type are called Labile.

"Metastable solutions always show smaller concentration than the labile solutions of the same substances. By increase of concentration,

* Lehrbuch, II. 2, 780–784.

therefore, a metastable solution goes over into a labile condition. The concentration at which the transition occurs is called the metastable limit.

"The metastable limit is, in the first place, dependent on the nature of the substances, on the temperature, and on the pressure. In addition it is influenced by various other circumstances not yet explained. At the present time (1899) it is hardly possible to speak more definitely concerning the value of the metastable limit and the methods of determining it."

It is in connection with this discussion in the Lehrbuch that Ostwald cites the sharpness and regularity of Liesegang's rings as evidence that the metastable limit is something definite. But so far as we are aware, no attempt has hitherto been made to study Liesegang's rings quantitatively, and to obtain from them the actual numerical value of the metastable limit. In fact, so far as we are aware, there has not been published a determination of the metastable limit in any case. We quote further Ostwald's explanation* of the formation of Liesegang's ring-system: —

FIGURE 2.

"By the diffusion of the silver salt into gelatine containing chromate a solution is formed which is supersaturated with respect to silver chromate; precipitation does not take place until the metastable limit has been exceeded. This naturally happens simultaneously in a circle concentric with the drop. Silver chromate, in relation to which the neighborhood of the ring is supersaturated, deposits on the precipitate already formed and strengthens it; this continues until the soluble chromate has been removed from the neighborhood and deposited on the precipitate. The silver salt, diffusing on farther, supersaturates a new circular region, and the process repeats itself. Since the silver nitrate becomes more dilute by diffusion, the critical concentration, at which precipitation begins, is reached later and later, and the rings form farther and farther apart."

Liesegang has also shown that if the potassium chromate in gelatine is put into a capillary *tube* instead of being spread upon a plate, analogous phenomena occur when one end of the tube is dipped into a solution of silver nitrate. The precipitate in the tube is formed in layers, or discs, perpendicular to the axis of the tube. (Figure 2.)

* Lehrbuch, II. 2, 778.

This phenomenon of the formation of a precipitate in rings on a plate or in discs in a tube is not confined to the case of a reaction between silver nitrate and potassium chromate. Liesegang found such a formation of a precipitate in the case of mercurous chromate, lead chromate, and Prussian blue, in the familiar reactions which give these precipitates. We have found that with a proper choice of concentrations rings are also formed in the following cases: —

TABLE I.

Diffusing Subs.	Subs. in Gel.	Precip.	Nature of Rings.
$Pb(NO_3)_2$	Na_2SO_4	$PbSO_4$	Fine. White. Close together.
$AgNO_3$	$K_2C_2O_4$	$Ag_2C_2O_4$	" " "
$AgNO_3$	Na_2CO_3	Ag_2CO_3	Thick. Far apart.
$AgNO_3$	Na_2HPO_4	$Ag_4P_2O_7$	Fine. White.
$AgNO_3$	NH_4CNS	AgCNS	" "
$AgNO_3$	KBr	AgBr	" "
$Co(NO_3)_2$	NaOH	$Co(OH)_2$	Gelatinous. Thick.
$BaCl_2$	$K_2C_2O_4$	BaC_2O_4	Distinctly crystalline.
$HgNO_3$	KBr	HgBr	Fine. White.
$FeCl_3$	Na_2CO_3	CO_2	Gas bubbles.

It is our intention to give a more extended description of the various reactions in this table at some future time. At present, however, in order to discuss the quantitative aspect of the problem, we shall confine our attention to a single case, — the formation of supersaturation rings of silver chromate.

The experiment was as follows: A capillary tube of diameter .5 to 1 mm. was filled with a $\frac{1}{75}$ or a $\frac{1}{150}$ normal solution of potassium chromate in gelatine. After the gelatine had set, a piece of the tube about 5 cm. long, obtained by breaking the tube under water so as to expose a fresh moist surface of the gelatine, was plunged vertically into a water solution of 2N, N or $\frac{N}{2}$ $AgNO_3$ contained in a flat-walled glass vessel. By means of a cathetometer carrying a microscope of low power we watched the formation of the precipitate. After a certain period of time, depending on the concentration of the solution, the precipitate near the

advancing front of the diffusing substance began to appear in layers, or discs, widely separated in comparison with their thickness. These discs appeared suddenly as a sharp, thin film, so that the *time* of their appearance could be determined with accuracy. The *distance* of each disc from the bottom of the tube was read off on the cathetometer. Measurements so obtained are recorded in the appended tables, IV to XXIV. The experiment was conducted in a constant-temperature room, which, except for the short time necessary for the taking of readings, was kept dark, or dimly lighted, to exclude the possible action of light in hardening the gelatine.

The reaction is in accordance with the formula:

$$2AgNO_3 + K_2CrO_4 \leftrightarrows Ag_2CrO_4 + 2KNO_3$$

The advance of the reaction in the one sense or the other is conditioned upon the concentration of the active substances. For equilibrium the concentrations must satisfy the quantitative relation:

$$\overset{+}{Ag}^2 \times \overset{--}{CrO_4} = K \,.\, Ag_2CrO_4 \qquad (a)$$

where $\overset{+}{Ag}$ and $\overset{--}{CrO_4}$ are the concentrations of the silver ion and the chromate ion respectively, Ag_2CrO_4 the concentration of the undissociated silver chromate in solution, and K the equilibrium constant. When the solid phase is present the undissociated silver chromate in solution must be in equilibrium with the solid phase, and must, therefore, be present in constant amount. In saturated solution, therefore,

$$\overset{+}{Ag}^2 \times \overset{--}{CrO_4} = k, \qquad (1)$$

where k is the *solubility product.*

Now in supersaturated solution the mass law (Eq. *a*) is probably still true, and the question arises; is there a relation similar to (1), with, however, a different constant product that defines the limit of supersaturation?

Is there a formula of the form

$$\overset{+}{Ag}^2 \times \overset{--}{CrO_4} = H \qquad (2)$$

for the condition that the concentrations must satisfy when the precipitate just begins to form in the *absence* of the solid phase?

II. Theoretical Considerations.

We can calculate the value of H in equation (2) provided we can calculate the values of the concentrations of the two ions at the point and at the time at which a ring begins to appear. We propose to attempt to obtain the values of these concentrations by the mathematical theory of diffusion. To avoid possible confusion from the use of general terms we shall take the specific case in which silver chromate is the precipitated substance; the same analysis will, of course, apply to any other case.

Suppose a capillary tube (Figure 3), containing in gelatine a dilute solution of potassium chromate, to be plunged at the time $t = 0$ into a vessel containing a strong solution of silver nitrate; let the distance x be measured from the end of the tube, with its positive direction along the axis of the tube; let u be the concentration of the $\overset{+}{Ag}$ ion at the point x at the time t, v the corresponding value for the $\overline{\overline{CrO_4}}$ ion. At the instant the tube is plunged in, that is, at the time $t = 0$, u is equal to U_0 for all negative values of x, and 0 for all positive values of x. Let 0 and V_0 be the corresponding initial values of v.

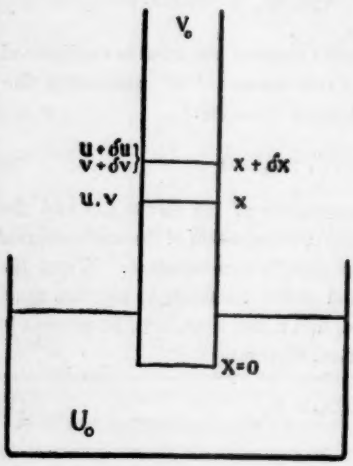

Figure 3.

As a first approximation we may assume that the dissociation of the K_2CrO_4 is complete, since this substance is present in very dilute solution for values of x and t such as we shall need to consider; the concentration of the silver salt in the tube will also be small, and we shall at present consider it to be completely dissociated. Later we can see how to correct the error introduced by this assumption. Thus if we measure concentration in gram-molecules, the concentration of the $\overset{+}{Ag}$ ion is the same as that of the $AgNO_3$, and the concentration of the $\overline{\overline{CrO_4}}$ ion is that of the K_2CrO_4. We are to calculate the two concentrations from the diffusion of $AgNO_3$ and K_2CrO_4.

The diffusion constant is defined as the number of units of mass that

will go through a unit cross-section in a unit of time under head of unit gradient of concentration. Let a^2 (essentially positive) be the diffusion constant of silver nitrate; then the quantity of silver nitrate that will cross a section s of the tube at a distance x from the origin in a time δt is the diffusion constant × gradient × time × area of cross-section. Therefore

$$Q = -a^2 \frac{\partial u}{\partial x} . \delta t . S \tag{3}$$

The quantity crossing a section at distance $x + \delta x$ is

$$Q + \frac{\partial Q}{\partial x} \delta x = -a^2 \frac{\partial u}{\partial x} \delta t \, S - a^2 \frac{\partial^2 u}{\partial x^2} . \delta t . \delta x . S \tag{4}$$

The accumulation of silver nitrate in the region between x and $x + \delta x$ is the difference of these quantities,

$$a^2 \frac{\partial^2 u}{\partial x^2} . \delta t . \delta x . S$$

This accumulation may also be expressed as change of concentration multiplied by the volume, $= \delta u . \delta x . S$;

$$\therefore a^2 \frac{\partial^2 u}{\partial x^2} \delta t . \delta x . S = \delta u . \delta x . S;$$

whence, dividing by $\delta t . \delta x . S$

$$a^2 \frac{\partial^2 u}{\partial x^2} = \frac{\partial u}{\partial t} \tag{5}$$

This is Fick's Law.*

Analogous considerations give us an exactly similar equation for the concentration of the $\overline{\overline{CrO_4}}$ ion at the point x and time t; namely,

$$b^2 \frac{\partial^2 v}{\partial x^2} = \frac{\partial v}{\partial t} \tag{6}$$

where b^2 is the diffusion constant for potassium chromate.

In deriving these equations we have made the assumption that the formation of earlier precipitates does not materially affect the head under which the ions accumulate for the formation of new precipitates. If we make this assumption we can solve the problem completely.

Equations (5) and (6) are exactly alike, but their solutions will be different because they have to satisfy different initial conditions in the two cases. The lower end of the tube was kept constantly, by occasional

* Pogg. Ann., XCIV. 59 (1855).

stirring, at the concentration U_0, so that equation (5) must be solved subject to the condition $u = U_0$ when $x = 0$ for all values of t, and $u = 0$ for all positive values of x at the time $t = 0$. Equation (6) has for initial values $v = V_0$ for all positive values and $v = 0$ for all negative values of x when $t = 0$. The theory of differential equations of this type teaches us that if we can obtain any one solution for each of these equations that satisfies its boundary conditions it is the only solution. The following are unique solutions of (5) and (6) subject to these conditions:

$$u = \frac{2U_0}{\sqrt{\pi}} \int_{\frac{x}{2a\sqrt{t}}}^{\infty} e^{-\beta^2} d\beta, * \tag{7}$$

$$v = \frac{V_0}{\sqrt{\pi}} \int_{\frac{-x}{2b\sqrt{t}}}^{\infty} e^{-\beta^2} d\beta, † \tag{8}$$

in which β is merely a variable of integration.

These may be seen to be solutions of (5) and (6) respectively if we differentiate them according to the rules for the differentiation of a definite integral and substitute the results in (5) and (6). Equation (7) is also seen to satisfy the initial conditions, for if $t = 0$ and x is positive, the lower limit of integration becomes $+\infty$, which is the same as the upper limit; the integral is therefore 0 and $u = 0$. If $x = 0$ the lower limit is 0 and the value of the integral is $\frac{\sqrt{\pi}}{2}$

$$\therefore u = U_0$$

Similar reasoning shows equation (8) to satisfy initial conditions for v.

The *metastable product* H, as we have defined it on page 8 (Eq. 2), should be given by the following equation:

$$H = u^2 v = \frac{4U_0^2 V_0}{\pi^{\frac{3}{2}}} \left[\int_{\frac{x}{2a\sqrt{t}}}^{\infty} e^{-\beta^2} d\beta \right]^2 \cdot \int_{\frac{-x}{2b\sqrt{t}}}^{\infty} e^{-\beta^2} d\beta \tag{9}$$

It is our problem to ascertain whether H is a constant for several initial concentrations of U_0 and V_0.

If we knew the diffusion constants a^2 and b^2 we could expand the integrals in (7) and (8), integrate term by term for a given value of x and t, and thus obtain u and v and from them H. This would necessitate a previous independent determination of the diffusion constants, and would

* Fourier, Th. an. de Chaleur, § 366 (1822).

† Fourier, loc. cit.; Stefan, Wiener Sitzungsber., 79, II. 176 (1879).

beside be very laborious, as the series do not begin to converge until after the sixth or seventh term. The difficulty of the series expansion might, however, be obviated by the employment of tables that have been computed for the definite integral.

We have employed a method in which a previous independent determination of the diffusion constants was not necessary. Before passing to the solution we shall call attention to an important and easy deduction from equation (9). In order for H to be a constant the lower limits of integration

$$\frac{x}{2a\sqrt{t}} \text{ and } \frac{-x}{2b\sqrt{t}}$$

should be constant for all rings in a given tube with given initial values of U_0 and V_0, and since a and b are constants $\frac{x}{\sqrt{t}}$ should be a constant. That is, for example, if we plunge a tube containing potassium chromate in gelatine into a solution of silver nitrate and observe with a cathetometer the distance from the bottom of the tube at which each thin disc of precipitate appears, and note, at the same time, the number of seconds that have elapsed since plunging in the tube, the distance divided by the square root of the time is a constant for all the discs in this tube, and for all tubes with the same initial concentrations of the reacting substances. The sample set of results given in Table II and all the tables, IV to XXIV (pp. 643–648), show with what consistency this conclusion is verified.

III. Determination of the Diffusion Constant and the Metastable Limit.

This constancy of $\frac{x}{\sqrt{t}}$ for any one set of observations under given conditions does not show, when taken alone, that there is a constant metastable solubility product H, but does show that, for a given concentration of one of the ions, there is a definite concentration of the other ion that will cause precipitation.

In order to examine into the constancy of H, the product of ionic concentrations as defined by equation (9), we shall need to employ the data furnished by different initial concentrations of the reacting substances, as collected in Table III, p. 635.

Every two sets of initial concentrations, together with the corresponding values of $\frac{x}{\sqrt{t}}$, will give the data for calculating the diffusion constant

TABLE II.

TEMP. 15.7. SILVER NITRATE, N. POTASSIUM CHROMATE, $\frac{N}{75}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1245	.537	.01522
1420	.575	.01526
1607	.611	.01524
1825	.649	.01519
2068	.694	.01526
2345	.738	.01524
2658	.785	.01523
3000	.834	.01523
3395	.888	.01524
3823	.940	.01520
4305	.998	.01521
4842	1.056	.01518
5443	1.125	.01524
6102	1.188	.01520
6870	1.260	.01520
		.01523
Mean error		.00002

a^2 and the value of H, as defined by equation (9). For example, if we substitute for U_0, V_0, and $\frac{x}{\sqrt{t}}$, the respective values of these quantities in sections (a) and (b) of Table III., we obtain the two following equations: —

$$H = \frac{4 \cdot 2^2 \cdot \frac{1}{75}}{\pi^{\frac{3}{2}}} \left[\int_{\frac{.0167}{2a}}^{\infty} e^{-\beta^2} d\beta \right]^2 \cdot \int_{\frac{-.0167}{2b}}^{\infty} e^{-\beta^2} d\beta. \qquad (10)$$

$$H = \frac{4 \cdot 1^2 \cdot \frac{1}{75}}{\pi^{\frac{3}{2}}} \left[\int_{\frac{.0153}{2a}}^{\infty} e^{-\beta^2} d\beta \right]^2 \cdot \int_{\frac{-.0153}{2b}}^{\infty} e^{-\beta^2} d\beta. \qquad (11)$$

TABLE III.

RECAPITULATION FROM TABLES IV–XXIV.

Silver Nitrate 2N *diffusing into*

(a) Potassium Chromate, $\frac{N}{72}$.

Table.	Temp.	$\frac{x}{\sqrt{t}}$
IV.	16.0	.01656
V.	16.3	.01663
VI.	16.3	.01671
VII.	16.1	.01700
Mean		.01670

Silver Nitrate N *diffusing into*

(b) Potassium Chromate, $\frac{N}{72}$.

Table.	Temp.	$\frac{x}{\sqrt{t}}$
II.	15.7	.01523
VIII.	15.5	.01524
IX.	17.0	.01549
X.	16.7	.01533
Mean . . .		.01530

(d) Potassium Chromate, $\frac{N}{150}$.

Table.	Temp.	$\frac{x}{\sqrt{t}}$
XI.	17.3	.01462
XII.	16.3	.01466
XIII.	16.7	.01467
XIV.	16.5	.01462
XV.	15.5	.01453
XVI.	16.6	.01477
XVII.	16.6	.01468
Mean . . .		.01465

Silver Nitrate $\frac{N}{2}$ *diffusing into*

(c) Potassium Chromate, $\frac{N}{72}$.

Table.	Temp.	$\frac{x}{\sqrt{t}}$
XVIII.	16.6	.01384
XIX.	16.8	.01377
Mean . . .		.01380

(e) Potassium Chromate, $\frac{N}{150}$.

Table.	Temp.	$\frac{x}{\sqrt{t}}$
XX.	17.7	.01311
XXI.	16.9	.01292
XXII.	16.0	.01335
XXIII.	15.5	.01313
XXIV.	15.5	.01299
Mean . . .		.01310

These two equations must be solved as simultaneous. We have been able to do this by the aid of a set of definite integrals given in the appendix of Kramp's *Analyse des Refractions Astronomiques et Terrestres*, published at Strassburg in 1799. Kramp's table contains values of the integral

$$\int_a^\infty e^{-\beta^2} d\beta$$

for 301 values of a from 0 to 3.00. This table shows, in the first place, that various values of

$$\int_{\frac{-x}{2b\sqrt{t}}}^\infty e^{-\beta^2} d\beta,$$

obtained on the assumption that b^2 is of the order of magnitude of the diffusion constant of an electrolyte, and that $\frac{x}{\sqrt{t}}$ is of the order of magnitude given by our experimental data, differ from each other and from $\sqrt{\pi}$ by less than 2 per cent. This means merely that the change of concentration, v, of the substance originally in the gelatine can be neglected.

Dividing equation (11) by equation (10), and extracting the square root, we have

$$\frac{\int_{\frac{.0153}{2a}}^\infty e^{-\beta^2} d\beta}{\int_{\frac{.0167}{2a}}^\infty e^{-\beta^2} d\beta} = 2. \qquad (12)$$

To solve this equation for a it is only necessary to find two values in Kramp's table for which the lower limits of integration are in the ratio 0.0167 to 0.0153, and for which the value of the integral corresponding to the second is double the value of the integral corresponding to the first.

To give an idea of the procedure in such a calculation we shall give on the next page a few values from Kramp's table in the neighborhood of the solution, of which the *starred* value is seen to be the one satisfying equation (12).

The ratio of 0.0167 to 0.0153 is 1.091.

a and a_1 are the lower limits of integration, A and A_1 the corresponding values of the integral. The correct solution is singled out by the relation $\frac{A}{A_1} = 2$,

a.	a_1.	$\frac{a_1}{a}$.	A.	A_1.	$\frac{A}{A_1}$.
1.77	1.932	1.091	.010909	.005677	1.921
1.79	1.954	1.091	.010067	.005077	1.983
1.80*	1.965	1.091	.009668	.004837	1.999
1.81	1.975	1.091	.009284	.004632	2.005
1.83	1.999	1.091	.008555	.004164	2.055

from which the value of a that most nearly satisfies equation (12) is seen to be 1.80.

$$\therefore \frac{.0153}{2a} = 1.80$$

$$a = 4.25 \times 10^{-3}.$$

The corresponding value A of the integral is .009668.
Therefore from equation (11)

$$H = \frac{4}{75\pi}(.009668)^2 = 1.6 \times 10^{-6}\left(\frac{\text{Gm. Mol.}}{\text{liter}}\right)^2.$$

The diffusion constant is not a, but a^2, which, reduced to the usual units with the day as unit of time by multiplying a^2 by 8.64×10^4, becomes

$$a^2 = 1.56\left(\frac{\text{cm}^2}{\text{day}}\right).$$

In this calculation of H the reacting substances have been assumed to be completely dissociated. The result of the calculation shows that the concentration of the silver ion was about $\frac{1}{200}$ Normal and that of the chromate ion $\frac{1}{75}$ Normal when precipitation occurred. The dissociation of $\frac{N}{200}$ silver nitrate differs so little from that of $\frac{N}{400}$, which enters into the calculation of subsequent cases, that the assumption of its complete dissociation introduces no appreciable inaccuracy. On the other hand, the dissociation of $\frac{N}{150}$ potassium chromate is about 1.05 times the dissociation of $\frac{N}{75}$, and this factor representing the ratio of dissociation must be introduced into calculations involving different concentrations of potassium chromate in the gelatine.

Observing this precaution we obtain the following values for a^2 and H from other sets of data of Table III.

FOR THE DIFFUSION CONSTANT OF SILVER NITRATE AND THE METASTABLE SOLUBILITY PRODUCT OF SILVER CHROMATE IN GELATINE AT 16° C.

From Table III. Data.	Diffusion Constant. $\frac{cm^2}{day}$.	Metastable Product. $\left(\frac{Gm.\ Mol.}{Liter}\right)^2$.
(a) and (b)	1.56	1.6×10^{-6}
(b) and (c)	1.56	1.6×10^{-6}
(a) and (c)	1.56	1.4×10^{-6}
(d) and (e)	1.53	1.3×10^{-6}
(b) and (d)	1.50	1.1×10^{-6}
(c) and (e)	1.53	1.3×10^{-6}
Mean	1.54	1.4×10^{-6}

IV. RESULTS.

Discussion of Results. — The values obtained for the diffusion constant and for the metastable solubility product are constant within the limit of error of the method, as will be seen by a reference to the recapitulation of Table III. While the value of $\frac{x}{\sqrt{t}}$ for any particular tube is constant within one or two tenths of one per cent, the same good agreement is not obtained when several series of observations are made upon different tubes under as nearly as possible the same conditions. The mean deviation of different tubes from the average is as great as one per cent. We think this deviation can be accounted for by lack of uniformity in the bore of some of the tubes, so that the diffusion takes place in a conical cavity instead of in a truly cylindrical cavity, as the theory requires. That an error of one per cent in the determination of $\frac{x}{\sqrt{t}}$ will account for the variations in the values of a^2 and H may be seen by a glance at the result of a recalculation of these quantities from the data (d) and (e) of Table III, on the assumption that the correct value of $\frac{x}{\sqrt{t}}$ in (e) is .0130 instead of .0131; a^2 comes out to be 1.63 $\frac{cm^2}{day}$, and H becomes 1.9×10^{-6}. Or, assuming $\frac{x}{\sqrt{t}}$ to be .0132 instead of .0131, a^2 becomes 1.42 and H becomes 0.7×10^{-6}.

In view of this sensitive dependence of the diffusion constant and the metastable product on the value of $\frac{x}{\sqrt{t}}$, we consider the results to be satisfactorily consistent.

We have not been able to find elsewhere any determination of the value of the diffusion constant of silver nitrate in gelatine. F. Voigtlaender* has found that the diffusion constants of salts in agar from his own measurements are in some cases smaller, in others equal to or larger than the corresponding constants for water solutions, the solutions employed having varying concentrations. He says that the question whether the diffusion in agar and water is identical can only be answered by further observations on pure water and other gelatinous solvents, such as water glass. Voigtlaender's measurements point to the conclusion, however, that the diffusion in agar and that in water are not very different, which makes our result for silver nitrate, 1.54, seem rather high, as the values obtained by Kawalki† would be for silver nitrate at 16° C. 1.13 to 1.20. Calculation of the diffusion constant for silver nitrate by Nernst's formula

$$a^2 = 0.0477 \times 10^7 \frac{u\,v}{u+v}\,[1 + 0.0034\,(t^\circ - 18)]$$

gives the value 1.29.

It should be noted that the value we have obtained is for diffusion through gelatine containing a rather heavy solid precipitate of silver chromate, and should not, therefore, be expected to agree with diffusion in water or pure gelatine. The important fact for this discussion is that a^2 is a constant and that there is hence no inconsistency in the conclusion that the metastable solubility product of silver chromate in gelatine is a definite constant quantity satisfying the relation

$$H = \overset{+}{\mathrm{Ag}}{}^2 \times \mathrm{Cr}\overset{--}{\mathrm{O}}_4.$$

As to the value of H, there are no other determinations of this quantity with which we might compare our results. As far as we know there have not been published any numerical data as to the value of the metastable product in any case. The ordinary solubility product of silver chromate in saturated water solution in the presence of the solid phase is 5.1×10^{-18} as determined by Kohlrausch.‡ The concentrations

* Zeit. Phys. Chem., III. 317 (1889).

† W. A., LII. 300 (1894).

‡ Leitver. d. Elektrolyten, p. 202.

of Ag_2CrO_4 in the two cases are in the ratio $\frac{\sqrt[3]{1.4 \times 10^{-6}}}{\sqrt[3]{5.1 \times 10^{-18}}}$. This means that the supersaturated gelatine at the concentration of precipitation held in solution 145 times the amount of silver chromate required to saturate it in the presence of the solid phase.

Lobry de Bruyn * and Liesegang † have shown that in the case of a large number of substances, which, like the silver haloids, form amorphous precipitates, gelatine inhibits precipitation. This phenomenon is especially easy to observe and demonstrate in the case of colored substances like silver chromate and lead iodide. It is well known that electrolytes, whether or not they act chemically on the colloid, may cause the precipitation of a colloid from solution, and it might be supposed that the case we are discussing can be explained as such an action of the diffusing silver nitrate in throwing down colloidal silver chromate. We are of the opinion that this is not the case, because, first, precipitation is here sudden and not slow, as is the case when colloids are precipitated by electrolytes, and, second, in the several cases of different concentrations of the reacting substances, the precipitate is formed, not for a constant concentration of the diffusing electrolyte, but for a constant value of the product

$$\overset{+}{Ag}^2 \times \overset{--}{CrO_4}.$$

Purification of the Gelatine. The best commercial gelatine contains usually about two per cent of ash, consisting of phosphates and carbonates, both of which form insoluble compounds with silver. Although the silver salts of these radicals are more soluble than silver chromate, it was thought necessary to remove them and other salts as thoroughly as possible from the gelatine to avoid their possible influence on the precipitation of the silver chromate. This removal was effected by electrolyzing the gelatine between membranes of parchment paper at five hundred volts continually for a week, during which time the membranes and electrodes were frequently washed by a stream of distilled water. Specimens of gelatine so prepared gave but a trace of ash on ignition.

Liesegang in his original research on reactions in gelatine solutions in capillary tubes found two classes of rings: the heavy widely separated red deposits of silver chromate, and beyond these and between them

* Rec. trav. chim. Pays-bas, XIX. 236.

† Phot. Wochenblatt, p. 229 (1894).

another series, consisting of fine, microscopic white lines. According to Liesegang's description, when the time came for the formation of a new red line one of the fine white lines suddenly became yellow and grew broader, until it encompassed four of the white lines and developed into the dark red of silver chromate. Liesegang observed, however, that these white lines are not necessary for the formation of the red ones and are not present when chromate diffuses into gelatine impregnated with silver. We are of the opinion that these secondary white lines are due to the presence of impurities in the gelatine, since they appear with the same distinctness when silver nitrate diffuses into commercial gelatine to which nothing has been added. They did not appear in our purest electrolyzed gelatine. The addition of soluble chlorides, bromides, or iodides in very small quantities causes the white rings to appear. Figure 4 and Figure 5 show them between the larger lines of silver

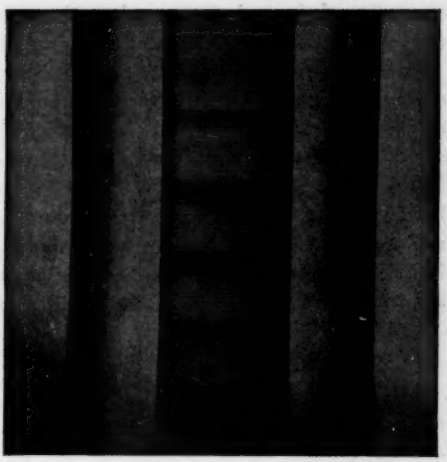

FIGURE 4.

Precipitation in commercial gelatine, showing fine white lines between the heavy dark deposits of $Ag_2 CrO_4$. This is a section of a tube like Figure 2, magnified 10 diameters.

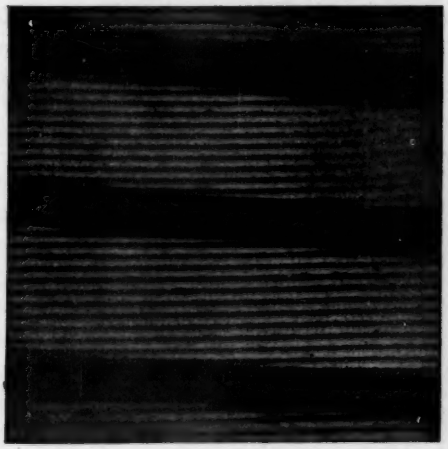

FIGURE 5.

Section of a plate like Figure 1, magnified 20 times, showing two sets of rings in commercial gelatine. The three heavy dark bands are Ag_2CrO_4.

chromate. It is our intention to investigate further the possible influence of impurities on the formation of these precipitates.

It is of interest to know that gelatine is not necessary for the production of rings, for when a very fine capillary tube filled with a water solution of potassium chromate is carefully plunged into a silver nitrate solution precisely similar phenomena may be observed. In this case, however, the layer of precipitate exists for only a short time after its formation. It breaks up under the influence of gravity and convection and mingles with the mass of silver chromate below. Three or four layers may exist at the same time, those of later formation being sharp, and the older ones gradually disintegrating into a mass of precipitate.

V. Conclusion.

We have shown by quantitative measurement that there exists in the case of the formation of silver chromate in gelatine solution a definite constant product

$$\overset{+}{Ag}^2 \times \overset{--}{CrO_4} = H$$

which determines the limit of supersaturation with respect to silver chromate in the absence of the solid phase.

Incidentally we have obtained a value for the diffusion constant of silver nitrate diffusing through gelatine containing solid silver chromate.

Jefferson Physical Laboratory,
Harvard University, Cambridge, Mass., U. S. A.,
March 1, 1903.

TABLE IV.

TEMP. 16.0. SILVER NITRATE, 2N. POTASSIUM CHROMATE, $\frac{N}{75}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1732	.687	.01650
1920	.723	.01650
2350	.801	.01652
2596	.845	.01659
2865	.888	.01659
3170	.934	.01659
3505	.982	.01659
3870	1.032	.01662
4315	1.083	.01652
4700	1.139	.01662
		.01656

TABLE V.

TEMP. 16.3. SILVER NITRATE, 2N. POTASSIUM CHROMATE, $\frac{N}{75}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1625	.672	.01667
1805	.705	.01660
2000	.742	.01660
2215	.782	.01662
2450	.822	.01661
2710	.866	.01663
2995	.910	.01663
3300	.955	.01663
3645	1.003	.01662
4020	1.051	.01658
4430	1.107	.01663
4885	1.162	.01663
5365	1.220	.01666
5895	1.280	.01667
		.01663

TABLE VI.

TEMP. 16.3. SILVER NITRATE, 2N. POTASSIUM CHROMATE, $\frac{N}{75}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1705	.684	.01657
1885	.719	.01655
2083	.760	.01662
2300	.798	.01665
2540	.842	.01671
3090	.930	.01673
3405	.976	.01673
3740	1.023	.01673
4110	1.077	.01680
4525	1.128	.01679
		.01671

TABLE VII.

TEMP. 16.1. SILVER NITRATE, 2N. POTASSIUM CHROMATE, $\frac{N}{75}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1580	.674	.01696
1750	.711	.01700
1940	.747	.01694
2150	.788	.01700
2385	.830	.01700
2625	.870	.01702
2910	.920	.01703
3215	.963	.01699
3550	1.015	.01704
3920	1.065	.01701
4320	1.117	.01700
4755	1.171	.01699
		.01700

TABLE VIII.

Temp. 15.5. Silver Nitrate, N. Potassium Chromate, $\frac{N}{75}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1530	.598	.01529
1745	.638	.01527
1985	.680	.01526
2564	.771	.01523
2903	.819	.01521
3290	.872	.01521
3720	.927	.01521
4210	.986	.01524
		.01524

TABLE IX.

Temp. 16.7. Silver Nitrate, N. Potassium Chromate, $\frac{N}{75}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1440	.585	.01535
1605	.619	.01545
1795	.655	.01546
2010	.695	.01551
2240	.734	.01551
2785	.819	.01551
3450	.911	.01551
3845	.964	.01555
		.01549

TABLE X.

Temp. 16.7. Silver Nitrate, N. Potassium Chromate, $\frac{N}{75}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1073	.498	.01520
1165	.523	.01532
1270	.546	.01532
1500	.594	.01534
1685	.622	.01538
1778	.649	.01538
1935	.675	.01535
2105	.706	.01539
		.01533

TABLE XI.

Temp. 17.3. Silver Nitrate, N. Potassium Chromate, $\frac{N}{150}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1332	.529	.01450
1535	.575	.01468
1790	.619	.01460
2090	.670	.01465
2422	.721	.01465
2830	.780	.01466
3280	.838	.01463
		.01462

TABLE XII.

TEMP. 16.3. SILVER NITRATE, N. POTASSIUM CHROMATE, $\frac{N}{150}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
800	.413	.01461
920	.443	.01461
1050	.473	.01459
1215	.508	.01456
1400	.548	.01465
1605	.586	.01463
1850	.631	.01466
2120	.675	.01466
2425	.724	.01470
2780	.775	.01470
3180	.830	.01471
3630	.884	.01466
4130	.949	.01475
4710	1.013	.01474
		.01466

TABLE XIII.

TEMP. 16.7. SILVER NITRATE, N. POTASSIUM CHROMATE, $\frac{N}{150}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1270	.520	.01459
1465	.557	.01454
1685	.602	.01466
1935	.645	.01466
2225	.694	.01471
2555	.743	.01470
2910	.794	.01471
3345	.847	.01465
3810	.908	.01471
4340	.970	.01472
		.01467

TABLE XIV.

TEMP. 16.5. SILVER NITRATE, N. POTASSIUM CHROMATE, $\frac{N}{150}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1225	.511	.01460
1410	.551	.01468
1653	.595	.01464
1930	.644	.01466
2243	.692	.01461
2606	.746	.01461
3028	.803	.01460
3500	.862	.01457
		.01462

TABLE XV.

TEMP. 15.5. SILVER NITRATE, N. POTASSIUM CHROMATE, $\frac{N}{150}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
965	.451	.01452
1108	.484	.01454
1295	.526	.01462
1505	.564	.01454
1745	.609	.01458
2025	.654	.01453
2345	.703	.01452
2702	.755	.01453
3115	.811	.01453
3595	.872	.01455
4165	.937	.01452
4770	1.002	.01451
5500	1.077	.01452
6380	1.155	.01448
		.01453

TABLE XVI.

TEMP. 16.6. SILVER NITRATE, N. POTASSIUM CHROMATE, $\frac{N}{150}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
945	.453	.01474
1090	.485	.01469
1260	.525	.01479
1460	.564	.01475
1685	.608	.01481
1950	.654	.01481
2250	.702	.01478
2605	.756	.01481
2995	.809	.01478
3440	.867	.01478
		.01477

TABLE XVII.

TEMP. 16.6. SILVER NITRATE, N. POTASSIUM CHROMATE, $\frac{N}{150}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1080	.479	.01458
1245	.515	.01462
1425	.554	.01468
1630	.592	.01466
1865	.637	.01475
2130	.679	.01467
2460	.725	.01468
2790	.780	.01477
3170	.833	.01479
. . .	. . .	. . .
10050	1.467	.01463
		.01468

TABLE XVIII.

TEMP. 16.6. SILVER NITRATE, $\frac{N}{2}$. POTASSIUM CHROMATE, $\frac{N}{75}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
905	.421	.01399
1105	.461	.01387
1210	.485	.01394
1333	.506	.01386
1468	.530	.01384
1765	.586	.01395
1985	.606	.01378
2120	.636	.01382
2316	.661	.01374
1543	.693	.01374
2780	.726	.01377
		.01384

TABLE XIX.

TEMP. 16.8. SILVER NITRATE, $\frac{N}{2}$. POTASSIUM CHROMATE, $\frac{N}{75}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1625	.555	.01377
1870	.596	.01378
2145	.640	.01382
2460	.683	.01376
2820	.734	.01382
3294	.784	.01366
3705	.839	.01379
		.01377

TABLE XX.

TEMP. 17.7. SILVER NITRATE, $\frac{N}{2}$. POTASSIUM CHROMATE, $\frac{N}{150}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1026	.420	.01311
1244	.460	.01304
1510	.508	.01307
1819	.558	.01308
2181	.614	.01315
2625	.672	.01312
3185	.740	.01311
3850	.819	.01320
4700	.901	.01314
5720	.988	.01307
		.01311

TABLE XXI.

TEMP. 16.9. SILVER NITRATE, $\frac{N}{2}$. POTASSIUM CHROMATE, $\frac{N}{150}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
705	.346	.01274
860	.380	.01296
1048	.419	.01294
1282	.465	.01298
1535	.508	.01297
1862	.559	.01295
2250	.614	.01295
2715	.674	.01293
3250	.734	.01288
		.01292

TABLE XXII.

TEMP. 16.0. SILVER NITRATE, $\frac{N}{2}$. POTASSIUM CHROMATE, $\frac{N}{150}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
1305	.434	.01340
1560	.529	.01340
1880	.580	.01337
2270	.633	.01329
2730	.697	.01334
3270	.761	.01331
		.01335

TABLE XXIII.

TEMP. 15.5. SILVER NITRATE, $\frac{N}{2}$. POTASSIUM CHROMATE, $\frac{N}{150}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
933	.400	.01310
1120	.440	.01315
1340	.481	.01314
1590	.525	.01317
1900	.572	.01312
2265	.625	.01310
2690	.681	.01313
3190	.742	.01314
		.01313

TABLE XXIV.

TEMP. 15.5. SILVER NITRATE, $\frac{N}{2}$.
POTASSIUM CHROMATE, $\frac{N}{150}$.

t sec.	x cm.	$\frac{x}{\sqrt{t}}$
900	.387	.01290
1080	.427	.01299
1300	.465	.01290
1565	.513	.01297
1875	.564	.01303
2235	.615	.01301
2670	.674	.01305
3180	.738	.01306
		.01299